Mechanical Mixtures of Me (Ni, Pd) Ce Oxides and Silica-Supported Heteropolyacids: Role and Optimal Concentration of Each Active Species in n-Hexane Isomerization

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Mechanical mixtures of Me(Ni,Pd)Ce oxides and silica-supported heteropolyacids : role and optimal content of each active species for n-hexane isomerization.

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Abstract - Catalytic properties of silica-supported heteropolyacids (HPA) in a mechanical mixture with reduced Me-Ce oxides (Me=Ni, Pd) in n-hexane isomerization are studied. The role of each component of the mixed oxides (Ce and, typically Ni and Pd) ,and their optimum content were enlightened; cerium, not only is beneficial for eliminating or prevent, the coke deposition but is also effective for maintaining the Keggin structure of the highly-organized HPA during the reaction and, probably allows a better dispersion of the second metal species. Nickel and palladium, present as Ni^0 and Pd^0 reinforce the activation of the alkane which is difficult to obtain by directly attacking by an acid and, thus, enhance noticeably the activity of the catalyst. The best mechanical mixtures are obtained with 30-70 wt % NiCeO-HPW/SiO_2 and 50-50 wt % $Pd_{0.1}$CeO-HPW/SiO_2.These mixtures have the highest efficiency for a Ni/Ni+W atomic ratio of 0.66 and a Pd/Pd+W ratio of 0.40 respectively. At last the conversion of n-hexane is in the order: HPW>HSiW>HBW which seems consistent with the order of their acid strength as claimed in the literature, but the isomerization selectivity appears slightly higher on HSiW.

Introduction

It is well-known that isomerization of light n-alkanes, which leads to branched alkanes, is easier on a bifunctional catalyst [1] by the help of a synergetic effect. Indeed, such a catalyst has hydrogenating/dehydrogenating and one another which is an acidic function. Both are working simultaneously as it is claimed that alkanes are dehydrogenated on metallic sites to the corresponding alkenes which are isomerized by acidic sites into branched alkenes; the latter are then hydrogenated into the branched alkanes again on the metallic sites. The mechanism can be different on mechanical mixtures, sometime called hybrid catalysts. As an example, Fujimoto et al [2] propose, on a physical mixture of Pt/SiO_2 and HZSM-5 powder, a mechanism based on a spillover phenomenon; the hydrogen gas being dissociated on tne noble metal before it spills over onto the zeolite. The spill over phenomenon has been put in evidence later by infra-red spectroscopy [3]. The spill over of the reactives species between metal promoted oxide systems and acid sites was also proposed by Vasina et al [4].

Generally, the metallic species, the more often used is platinum. Concerning the solid acids, many catalysts, different of the chlorinated alumina, were tested (e.g. zeolites [5], sulfated zirconia [6], tungsten/molybdenum oxides [7] and heteropolyacids [8]). In some cases, a third component was added to improve the role of the metallic species [9-12]. Due to the strong and amenability to "molecular tuning" acidity (through their salts), the heteropolyanions (HPA), which are highly organized systems, are very good candidates for co-catalyze n-alkane isomerization. Unfortunately, the Keggin structure can be easily destroyed when HPA are not protected. Ono and co-workers appear to be the first to incorporate palladium as metallic species to prevent such destruction [1] and, on the other hand, we have previously shown that cerium is capable to prevent the poisoning during some hydrogen treatments [13]). Moreover, very few works deal with the role and the influence of the content of each component in a mixture of metallic oxide and HPA. Thus, this work describes the results obtained on various mixed oxides and different HPA in a mechanical mixture and focus on the specific role of each component for the n-hexane isomerization.

Experimental

Heterophosphotungstic acid (HPW), heterosilicotungstic (HSiW) and heteroborotungstic (HBW) acids were prepared in a classical way [14]. Silica-supported hetropolyacids were prepared by the wet impregnation method. Ce-Ni oxides were prepared by the reverse homogeneous co-precipitation method as described in the literature [15]. Cerium nitrate $Ce(NO_3)_2.6H_2O$ (Prolabo Co) solution (0.5 $mol.L^{-1}$) and nickel nitrate $Ni(NO_3)_2.6H_2O$ (Prolabo Co) solution (0.5 $mol.L^{-1}$) were prepared separately and then mixed. The mixed solutions were added dropwise to an excess of potassium hydroxide KOH (Prolabo Co) solution ($0.5mol.L^{-1}$) under strong stirring. After filtration, the precipitates formed were washed with hot water (335 K) to eliminate K^+ until the pH value of the washing solution decreased from approximatly 11 to 7. The compounds were dried in an oven at 373 K for 12 hours, ground and calcined in air for 4 hours at 673K with a heating rate of 2 $K.min^{-1}$. The Ce-Pd oxides were prepared in the same manner from $Pd(NO_3)_2.6H_2O$ (Prolabo Co) solution (0.5 $mol.L^{-1}$). The samples placed into a flow reactor (U-type glass) were first reduced, at 498 K and 553 K for Ni-Ce-O and Pd-Ce-O respectively, for 4 h in hydrogen with a flowing rate of 21.8 $ml.min^{-1}$under atmospheric pressure, and then their catalytic properties were evaluated under the same conditions but hydrogen passed through a saturated containing n-hexane (WWH = 0.36 h^{-1}). The products were analyzed by gas chromatography [16].

Results and discussion

Owing to their very low surface area, pure heteropolyacids have a very poor activity. Thus, supported HPA, more particularly on silica, are used [17]. The conversion increases remarkably with the HPA loading although it remains low (table1). Unfortunately, the isomerization selectivity decreases simultaneously but, the yield of the C6 isomers and the ratio of the dimethyl butanes (DMB), by respect to the total amounts of the branched alkanes (dimethyl butanes -DMB- plus methyl pentanes -MP-) increase a little bit.

The main drawback of the silica-supported HPA alone is the rapid poisoning of the solid on time. As an example, after 22 min of reaction time, the conversion is already divided by a factor 4 (table2).

This deactivation, on HPA and their salts, was previously observed by Guisnet et al [18] who assume that this one is related to

Table1. Isomerization of n-hexane over x wt % HPW/SiO_2 after 5 min on stream at 498K.

x	10 wt %	20 wt %	30 wt %	40 wt %	50 wt %
% conversion	3.7	5.6	16.6	17.3	28
% isomerization	78	76.7	68	63.3	55.9
DMB/(DMB+MP) %	15.9	15.6	17	18	9
C6 isomers yield %	2.9	4.3	11.3	11	15.6

DMB = dimethyl butanes, MP = methyl pentanes

Table2. Isomerization of n-hexane over 40wt % HPW/SiO_2 on stream at 498K.

Time(min)	5	22	57
% Conversion	17.3	4.4	2.6
% isomerization	63.3	78.2	78.9
DMB/(DMB+MP) %	18	16	14
C6 isomers yield %	11	3.5	2

DMB = dimethyl butanes, MP = methyl pentanes

a coke formation but these authors worked in absence of hydrogen which is known to preserve a little this formation. Nevertheless, only presence of hydrogen is clearly not sufficient to avoid poisoning in our case. One alternative to correct these drawbacks is to add a co-catalyst capable to avoid the poisoning and to protect the highly organized catalytic system (viz: HPA). On the other hand, it is well known that isomerization reaction is easier in presence of a bifunctional catalyst [1] with one acidic function and one hydrogenating/dehydrogenating function; if HPA, which exhibit a strong acidity, are good candidates for the former function, a metallic species must be an excellent candidate for the second one. Presence of cerium was also proved to be favorable to prevent sulfur poisoning during hydrotreating reactions [13]. Ono and co-workers appear to be the first to incorporate palladium as a cation for the isomerization of n-alkanes[19] and it was previously reported that the reduced Ce-Ni mixed oxides could be used as promoters for the hydrogenation reactions[20]. So, we undertook the study of each component of a complex mixture to know what are the specific role of each active species, and the value of their optimal content. The table 3 displays the results obtained with mechanical mixtures of HPA/SiO_2 and Ni_xCe oxide or Pd_yCe oxide were x and y are the atomic ratio Me/Ce. No deactivation was observed, even after 4 h on stream. As expected, the only presence of cerium does not play an important role for the activity but prevent the poisoning of the HPA as, in absence of Ce, the activity decreases on time. Thus, the cerium, probably, is an electronic promoter due to the Ce^{4+}/ Ce^{3+} Red-Ox system which improves the rate of the reducibility of the nickel and palladium ions during the reaction. We have to recall that when the metallic species used is platinum, we do no longer observe poisoning, even in absence of cerium [8]. Misono et al [21] observed the same absence of deactivation on a mechanical mixture of Pt/SiO_2 – HPW cesium salt or sulfated zirconia or zeolite β as soon as the hydrogen pressure reached 0.2 atm. Concerning the ratio Ni/Ce, surprisingly, it appears little influencing the level of conversion when we double this ratio; but we observe an effect on the

Table3. Effect of the ratio Me/Ce on the catalytic properties of the mechanical mixture of Me-Ce-O and HPW/SiO_2

Ni/Ce ratio*	1	2
% conversion	27.7	26.2
% isomerization	91.2	96
DMB/(DMB+MP) %	17.9	15.1
C6 isomers yield %	25.3	25.1

Pd/Ce ratio**	0	0.05	0.1	0.15	0.2
% Conversion	13.3***	26.4	56.2	49.8	39
% isomerization	93.2	99.2	98.2	98.6	98.9
DMB/(DMB+MP) %	14	9.5	14.4	11.1	8.9
C6 isomers yield %	12.4	26.2	55.2	49.1	36.6

*mixture of $20\%Ni_xCeO$-80% ($50wt\%HPW/SiO_2$), **mixture of $50\%Pd_yCeO$-50 % ($20wt\%HPW/SiO_2$), *** conversion after few minutes. DMB = dimethyl butanes, MP = methyl pentanes

amount of DC6 obtained and the value of 1 appears the right ratio. The activity is more sensible to the ratio Pd/Ce as we can multiply by a factor 2 the activity, the best ratio seems to be 0.1.

XRD patterns of fresh and reduced solids are very interesting. For fresh Ni-Ce oxides we observe the XRD patterns of both NiO and CeO_2 compounds but the sample reduced at 498K shows new peaks which can be assigned to Ni^0 while the peaks of the NiO crystal disappear suggesting that most of the nickel oxide has been reduced in metallic species [12]. An identical result is observed with the mixed Pd-Ce oxide: simultaneous presence of PdO and CeO_2 on the fresh oxide and of Pd^0 after reduction at 553K [11]. Thus, Ni^0 and Pd^0 species are the active hydrogenating species for the n-hexane isomerization and, probably, the lower efficiency of nickel for such a reaction, partly due to the lower reaction temperature, can also be explained by the different behavior of the Me/Ce ratio. Thus, The ratio 1 and 0.1 for Ni/Ce and Pd/Ce respectively were chosen to pursue the studies.

The respective amounts of the mixed oxide and of HPA influence also the n-hexane reaction activities. For the nickel-based mixed oxide, the optimal amount of NiCe is 30% (table 4a), which does not corresponds exactly to the higher value of DC6 obtained while for the Pd-based oxide, the best mixture is constituted of 50% of $Pd_{0.1}CeO$ (table 4b) which corresponds to the larger DC6 percentage.

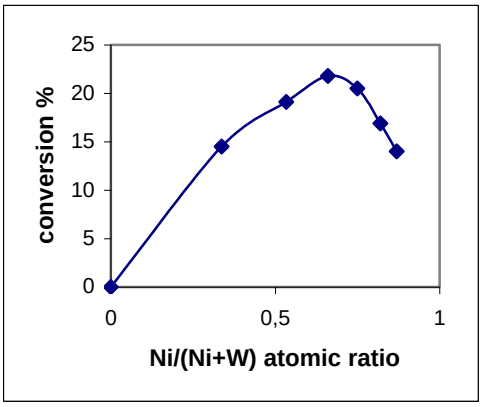
The figure 1 displays the n-hexane conversion versus the Ni/Ni+W (figure 1a) and Pd/Pd+W (figure 1b) atomic ratio. This ratio is really representative of the metallic sites/acidic sites relative amount, and consequently of the magnitude of the synergy phenomenon.

Table4a. Effect of the wt % of NiCeO mixed oxide on the catalytic properties of the mechanical mixture of Ni-Ce-O and (20 wt $\%HPW/SiO_2$).

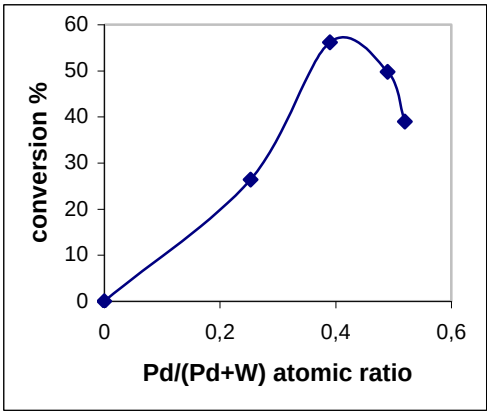
NiCeO wt%	10	20	30	40	50	60
% conversion	14.5	19.1	21.8	20.5	16.9	14
% isomerization	86.6	87.3	80.4	76.5	50.4	41.6
DMB/(DMB+MP) %	17	15	11	11	9	4
C6 isomers yield %	12.6	16.7	17.5	15.7	8.5	5.8

Table4b. Effect of the wt % of PdCeO mixed oxide on the catalytic properties of the mechanical mixture of Pd-Ce-O and (20 wt %HPW/SiO_2).

$Pd_{0.1}CeO$ %	25	40	50	60	75
% Conversion	20.8	47.8	56.2	48.7	5.7
% isomerization	98.9	98.5	98.2	98.5	93.7
DMB/(DMB+MP) %	6.8	13.3	14.4	13.5	4.3
C6 isomers yield %	20.6	47.1	55.2	48	5.3



1a



1b

Figure1. n-hexane isomerization conversion versus the tungsten content in the mechanical mixtures of MeCeO-HPW/SiO_2 (1a: NiCeO-20wt%HPW/SiO_2; 1b: $Pd_{0.1}$CeO-20wt%HPW)

Table5. Effect of the central atom in heteropolyacid for mechanical mixtures

HPA	HPW		HSiW		HBW	
MeCeO	NiCeO[a]	$Pd_{0.1}CeO$[b]	NiCeO[a]	$Pd_{0.1}CeO$[b]	NiCeO[a]	$Pd_{0.1}CeO$[b]
% Conversion	27.7	56.2	23.3	47	2.1	-
% isomerization	91.2	98.2	94.2	99.3	67	-
DMB/(DMB+MP) %	17.9	14.4	13.1	11.6	8	-
C6 isomers yield %	25.3	55.2	22	46.7	1.4	-

a: mixture of 20%NiCeO-80%(50wt%HPA/SiO_2). b: mixture of 50%$Pd_{0.1}$CeO-50%(20wt%HPA/SiO_2)

For NiCeO-HPW mechanical mixtures, the higher conversion is reached for about 66% moles of Ni by respect to the total (Ni+W), that is to say 2 moles of Ni per mole of W. For the $Pd_{0.1}$CeO-HPW mechanical mixtures, the best conversion is obtained with 40% moles of Pd by respect to the total (Pd+W), that means 0.66 mole of Pd per mole of W. Besides, these values can be linked with the number of easily accessible Me centers from or to the acid sites in term of proximity, and is comparable with those previously obtained by Alvarez *et al* on PtHY catalysts [22] and confirm the best hydrogenating nature of Pd. At this point, it seems interesting to study the influence of the central atom in the well-organized heteropolyacids. The table 5 shows the results obtained with HPW, HSiW and HBW respectively for the two kind of mechanical mixtures.

If the results with the borotungstic acid are definitely and drastically less interesting,

(we did not try it over $Pd_{0.1}CeO$), the conversion are in the order:

HPW> HSiW> HBW

which is consistent with the order of their acid strength as claimed in the literature [23]. However, this is not totally true for the isomerization selectivity which, slightly, is better on HSiW, probably because $SiW_{12}O_{40}^{4-}$ is a softer base than $PW_{12}O_{40}^{3-}$ complexing organic cation to form a stable intermediate.

In summary, we can now precise the role of each metallic species presenting in the catalyst. Cerium component has mainly a protective function avoiding the poisoning of the others elements. This protection origins probably by the Ce^{4+}/Ce^{3+} Red-Ox system which reinforces the protection of species as nickel as proposed by Sauvion *et al* [24]. In our reactions conditions, the main reaction products are methyl pentanes (MP) and dimethyl butanes (DMB). Guisnet et al [18] assume that, on pure HPA cesium salt, 2,3-DMB and MP are primary products formed by an intramolecular isomerization of a classical carbenium ion coming through a monomolecular mechanism. In the presence of a metallic species, the classical bifunctionnal mechanism is well admitted and explained in [21] justifying the necessary close proximity of the metal centers and of the acid sites for allowing the spill over of, either the hydrogen species or the one of the intermediates In this latter case, nickel and palladium, both in the metallic state, are the hydrogenating/dehydrogenating function and provide an important synergetic effect to HPA for the global transformation. The only requirement for such a synergy is a sufficient amount of the Me^0 species and a good dispersion of the various active species on the support. For the former condition, an amount of 2 Ni^0 atom and 0.66 Pd^0 atom respectively per tungsten atom appears as optimal for the two different mixed oxides (i.e. NiCeO and $Pd_{0.1}CeO$), and for the second condition, we can reasonably assumr that the 30-70 and the 50-50 mixtures are homogeneous. Besides, the tries with co-impregnated Pd_xCeO-HPA/SiO_2 give rise to the same range of order of conversion [2]. The last result is on the type of central atom for the HPA; we observe a higher activity with HPW than with HSiW or HBW. This is simply related to the acidic strength.

Conclusion

Mechanical mixtures of mixed Me-Ce oxides (Me=Ni, Pd) and silica-supported heteropolyacids (HPA= HPW, HSiW, HBW) have a beneficial effect on the n-hexane isomerization to branched alkanes. The primary beneficial effect, in term of synergism on the activity, can be explained by the more or less close proximity of the two important functions (i.e. hydrogenating/dehydrogenating function on the metallic species coming from the reduced mixed oxides and the acidic properties of the silica-supported heteropolyacid). The secondary beneficial effect is also important, more particularly for the Ni-based system; firstly, the Keggin structure, which is a highly organized structure, is maintained and secondly, the sensibility to coke deposition, and consequently to the decrease of the activity by poisoning, is totally inhibited. Thus a whole study of the best type of the different metallic species and of their optimal content shows that the best mixture is: 50wt% of $Pd_{0.1}Ce$ oxide and 50wt% of (20wt%HPW/SiO_2).

Acknowledgments

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